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APPLICATION OF SILVER RECOVERY TO THE ES-38 MOBILE PHOTOGRAPHIC--ETC(U)

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Research and Development Technical Report
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APPLICATION OF SILVER RECOVERY TO THE ES-38 MOBILE
PHOTOGRAPHIC PROCESSING LABORATORY

Joseph H. Zarzycki

Combat Surveillance & Target Acquisition Laboratory

October 1976



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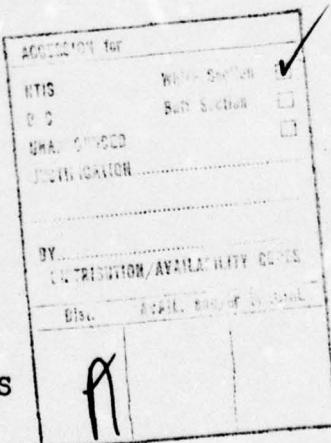
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report deals with the evaluation of silver recovery methods for use in the Mobile Photographic Processing Laboratory ES-38. Work done to date on silver recovery within the Army's other mobile photo processing laboratory, the ES-82, is summarized in a memorandum entitled "ES-82 Mobile Photographic Processing Laboratory Silver Recovery Method Evaluation," 20 June 1974. The retrofit of Army mobile photo labs with silver recovery devices is being funded under Product Improvement Program 1-73-07-139.		

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1. INTRODUCTION

a. ES-38B Processing

The ES-38B is a transportable, self-contained photographic darkroom used for processing black and white aerial film.¹ Developing, fixing, washing, and drying of exposed film and paper are accomplished by each of the two EH-29B processing machines. These processors handle 70mm, 5 inch or 9-1/2 inch films and 9-3/8 inch print paper; film is processed at between 1-1/2 and 7 feet/minute and paper is processed at 7 feet/minute. (See Figures 1 and 2 for outside and inside view respectively of the ES-38B Mobile Processing Laboratory. See Figure 3 for a view of the EH-29B Processor.)

Each EH-29B processor consists of a processing machine, EH-48B, and a temperature control unit, FH-6B. The EH-48B is comprised of four tanks, 5 gallon developing, 5 gallon fixing, 5 gallon hypo clearing and 8 gallon wash water, a drying compartment, pumps for agitation and circulation, solution temperature control devices, and a variable speed film and paper transport mechanism. The FH-6B temperature control unit houses a refrigeration and a heating system and operates in conjunction with the processing machine's heat exchanger.²

Presently the replenishment schedule for rapid fix requires that 1 gallon of fixer be dumped after processing every 200 linear feet of 9-1/2 inch film or equivalent (158 square feet) and that the tank then be topped up with fresh fixer. This procedure is followed until a total of 948 square feet of film (1200 linear feet of 9-1/2 inch film) has been processed, at which time the entire tank is drained and refilled with freshly mixed Eastman Kodak Rapid Fix. Similarly, the replenishment schedule requires 2 quarts of AFD No. 4 developer to be drained and then refilled every 158 square feet with a total draining to occur every 948 square feet. The hypo clearing tank and the wash water tank are completely drained and then refilled every 316 square feet (400 linear feet of 9-1/2 inch film).³

b. Product Improvement Program No. 1-73-07-139

The objective of Product Improvement 1-73-07-139 is to profitably remove silver from the fixing solution contained in the EH-29B processors. Silver is a valuable metal (present market price is approximately \$4.00 per

1 "Photographic Darkroom Group ES-38B and ES-38B1," TM-11-6740-282-12, Dept of the Army, HQDA, Washington, D. C., 22 May 1969.

2 "Processing Machine Photographic Film and Paper, EH-29B," TM-11-6740-278-12, Dept of the Army, HQDA, Washington, D. C., April 1969.

3 "Processing Instructions for Use with Processing Machine, Photographic Film and Paper, EH-29B," TB-11-6740-278-10/1, Dept of the Army, HQDA, Washington, D. C., 18 August 1971.

troy ounce) and recovery from scrap material is required by DOD Directive.⁴ The silver which is recovered from the used fixer solution will be furnished to the DOD Silver Program Manager for refining and then future use as Government Furnished Material.⁵

In addition to being economically recoverable, the removal of silver prior to dumping silver bearing effluents into the environment is necessary because silver in the ionic form, as found in photographic fixing baths, is toxic to both aquatic life and to the bacteria of waste treatment facilities. It was the intent of the PIP to remove the silver and simultaneously rejuvenate the fixing bath, thereby gaining the economics of less fixer usage and at the same time reducing the quantity of fixer dumped into the environment. This is also desirable in that the sulfite and thiosulfate found in the fixer are major contributors to the high oxygen demand of ES-38B effluent. (A waste stream having a high oxygen demand when dumped into a natural receiving water removes oxygen from that body and, thereby, robs aquatic life of the dissolved oxygen in the water which is needed for their survival).

The initial phase of the project called for the investigation and analysis of currently available silver recovery equipment and techniques. This phase is to be followed by the purchase and testing of equipments and the modification of silver recovery equipments and/or the internal shelter configurations.

c. Silver Recovery from Fixing Baths

Silver halide crystals are the light sensitive substances which are dispersed throughout the film's emulsion layer. When film is exposed to light, it is believed that a latent image is formed by the nucleation of silver particles in the areas exposed to the light. These nuclei serve as centers for the production of metallic silver grains when the film is subsequently developed in a chemical reducing solution. Those areas which have not been exposed do not have these nuclei and are essentially unaffected during development. When the developed film is immersed in a fixing bath, the undeveloped silver halides are dissolved away by the action of the fixer (ammonium thiosulfate in the case of the ES-38B); this undeveloped ionic silver remains in the fixer solution as a contaminant.⁶

⁴ "Reclamation and Utilization of Silver from Scrap Materials," DOD Directive 4160.22, Dept of Defense, Washington, D.C., 23 August 1968.

⁵ "Reclamation and Utilization of Silver from Scrap," DA Circular 755-12, Dept of the Army, HQDA, Washington, D.C., 19 December 1968.

⁶ M. J. Stiso, Jr., "Tactical Imagery Processing Laboratory (TIPL): Preliminary Considerations on Silver Recovery and Effluent Pollution Control," Research and Development Technical Report ECOM-3445, ECOM, Ft. Monmouth, NJ, p. 1, August 1971.

There are three readily available commercial methods of silver recovery from photographic fixing baths. These are precipitation, metallic replacement, and electrolysis. In addition to these methods, ion exchange and reverse osmosis techniques have been developed; although technically feasible, these methods are not economical at the present time.⁷

Precipitation methods include addition of sodium sulfide, sodium hydrosulfite, calcium hydroxide, or some other chemical agent which reacts with the silver or silver thiosulfate ion to form a sludge which can be filtered, dried, and then refined. This method requires the use of settling tanks and often gives off toxic fumes.⁸

In metallic replacement, fixer is brought into contact with a metal surface such as steel, copper, or zinc which replaces the dissolved silver. This method requires little space, no electrical connections, no settling, and little operator attention. Available commercial units utilize a steel filler material, such as steel wool, contained in a plastic cartridge through which spent fixer is fed.

In electrolysis a direct current is passed through the fix bath; the silver is plated out on the negatively charged cathode. This method allows reuse of fixer and yields high purity silver.

2. PROJECT PLANNING

The initial phase of the project was divided into two tasks to be accomplished simultaneously. Task one was to gain a total understanding of methods of silver recovery and to be familiar with all commercially available equipment. Of the commercially available methods for recovering silver from fixing solutions noted above, precipitation techniques were not considered in detail because, in the case of the ES-38B, they offer no substantial cost saving over the other two techniques and require more space and operator attention. Metallic replacement and electrolysis were investigated thoroughly.

Task two required working with the EH-29B processor and obtain information and data necessary for the specification of a silver recovery unit. The parameters studied were:

- a. Chemical characteristics of EH-29B exhausted fixer solutions effecting silver recovery efficiency, such as, silver concentration, sulfite concentration and pH.

⁷ "Recovering Silver from Photographic Materials," Kodak Pamphlet No. J-10, Eastman-Kodak Co., Rochester, NY, p. 21, 1969.

⁸ M. L. Schreiber, "Present Status of Silver Recovery in Motion Picture Laboratories - A Tutorial Paper," Journal Society of Motion Picture and Television Engineers, Vol. 74, p. 506, June 1965.

b. Work unit times, such as, mixing time, film loading time and processor draining time; this data was gathered to assure that silver recovery would not interfere with present mission performance capability.

c. EH-29B processing characteristics, such as, dilution effects caused by film carryout, fixer clearing time, and pumping and agitation capability.

d. ES-38B space availability.

The findings from these two tasks were to provide data for a trade-off analysis yielding the best method for silver recovery in the ES-38B. This analysis would also serve as the basis for the selection of commercial equipment for purchase and testing and for a preliminary design of the silver recovery system's interface with the shelter and the processor.

Subsequent project phases would then be test and evaluation, TECOM testing, preparation of procurement data for MWO kits, the contract phase and retrofit.

3. RESULTS

a. Hypo Regeneration

If an electrolytic silver recovery unit is connected to the hypo recirculation pump in the EH-48B processing machine, it is possible to pump fixer solution out of the bottom of the tank into a silver recovery cell and then through the processor's heat exchanger and back into the tank.

Such a system would still provide the needed circulation in the fixing tank and also provide continuous removal of silver. The silver concentration in the fix tank would be maintained at a low level and ammonium thiosulfate would be regenerated in the process.

It is also possible to regenerate hypo by the batch method. The contents of the fix tank would be pumped into an electrolytic silver recovery unit and allowed the necessary time for desilvering and then drained back into the processor. This approach offers no advantage over the recirculation system and in fact requires more space and is more time consuming.

Fixer life cannot be extended with the metallic replacement cartridge because the system substitutes a ferrous ion (Fe^{++}) for two silver ions (Ag^+) and, thereby, contaminates the hypo solution. Efficient use of the cartridge requires that the hypo solution flow slowly through the ferrous filler material allowing adequate time for the replacement of silver to occur. The EH-29B's fixing tank can be drained in approximately 5 minutes; to drain the fixer through the cartridge at this rate would result in almost no silver recovery. Therefore, in order to use a cartridge, it is necessary to drain the exhausted fixer into a holding tank and then slowly feed the fixer out of the tank and through the cartridge. If a 5 gallon holding tank is used to

feed fixer through an orifice and into the cartridge even at the most rapid processing rate (7 feet/minute), the prescribed feed rate of 300 milliliters/minute⁹ can be maintained through the cartridge without an overflow condition occurring and with no holdup in the processing resulting.

At the outset electrolytic silver recovery, utilizing a recirculating system, appeared to be the best approach offering continuous silver recovery with extension of hypo life. Testing to determine how much of a life increase could be expected uncovered some problems with this approach, however. The problem areas are: (a) carryout of chemicals on the film surfaces from one tank to the next, (b) formation of silver sulfide, and (c) the need for a high recovery capability when processing film at high speed.

First a control test was run with the processor in the normal configuration; this was followed by processing with an electrolytic unit connected to the fixer tank in the recirculation mode. It was the intent to compare these runs and measure the additional fixing capability obtained with continuous electrolytic silver recovery.

The Air Force in a report prepared by Goodyear Aerospace¹⁰ stated that a six fold increase in ammonium thiosulfate life was obtained with the employment of an Arenta electrolytic silver recovery system. Kodak¹¹ estimates that approximately a 20 percent ammonium thiosulfate life increase can be expected when electrolytic silver recovery is used.

b. Carryout

The EH-29B processor was operated at 7 feet/minute in both the control run and when processing with continuous silver recovery. This is the highest processing speed recommended for processing, and was selected because it represented the maximum rate at which silver would be generated in the fixing tank and the greatest rate at which solution would be carried out on the film surface. Testing indicated that at 7 feet/minute film carryout of solution was 0.25 ounce per linear feet of film processed (based on 9-1/2 inch film). This represents a significant dilution and contamination to the fix tank by carryout from the developing tank. With such a large amount of developer being carried into the fixing tank and an amount of fixer similarly being

⁹ "Silver Recovery with the Kodak Chemical Recovery Cartridge Type P and Type 3," Kodak Pamphlet No. J-9, Eastman-Kodak Co., Rochester, NY, p. 11, March 1972.

¹⁰ C. Trybus, J. McMasters, E. Cadiz, "Silver Recovery and Water Conservation for WS430B System," Goodyear Aerospace Corp., Ariz. Div., p. 4, May 1973.

¹¹ "Recovering Silver from Photographic Materials," Kodak Pamphlet No. J-10, Eastman Kodak Co., Rochester, NY, p. 18, 1969.

carried out into the hypo clearing tank, it was found that unless the rapid fix was replenished, clearing time, even with silver recovery, was unsatisfactory after 200 linear feet of processing.

Discussions with the Photo Optics Tech Area of the CS&TA Laboratory and review of a report prepared by that group entitled "Photographic Formulations for Machine Processing,"¹² revealed that for good results processing of film in the EH-29B at greater than 5 feet/minute was not recommended in most cases. Processing speeds of 7 feet/minute for duplication film and photographic printing paper are recommended.¹³ Although the Photo Optics Technical Report does not indicate why EH-29B fixing at high processing speeds is inadequate, it has been reported that fixing inadequacies were due to the short immersion time provided at higher than normal speeds. Data in that report is based on a replenishment schedule calling for 4 quarts of fresh fixer to be added for every 200 feet of 9-1/2 inch film processed. These results, therefore, were not useful in estimating whether hypo life extension at lower film speeds was achievable.

In order to measure the carryout effect when processing film at lower speeds, an additional 1200 feet of film were processed; 400 feet were processed at 1-1/2 feet/minute, 400 feet were processed at 3 feet/minute, and 400 feet were processed at 4-1/2 feet/minute. In each of these cases the carryout of developer was measured to be approximately the same as that experienced when processing at 7 feet/minute, i.e., 0.25 ounce of developer carried into the rapid fix tank per linear foot of 9-1/2 inch aerial film processed. It is noted that accumulation was not found in any of the tanks and, therefore, carryout was equivalent throughout the processor.

The effect of carryout when processing photographic print paper was also studied. Twelve hundred linear feet of 9-3/8 inch photographic print paper was processed at 7 feet/minute. Carryout averaged 0.14 ounce of developer carried over per linear foot of 9-3/8 inch print paper processed.

The carryout of solution from the fixer tank causes a spill over of silver which has been fixed out of the film or paper into the hypo clearing tank (tank #3). This was not expected to be significant. It was initially estimated that 5 percent \pm 2 percent of the undeveloped silver from the film being processed would be carried into the hypo clearing and wash water tanks; this figure was based on the average silver concentration in the fixer tank during processing and the solution carryout rate. Analysis of the test samples, however, showed that when processing Plus-X Aerecon film at 7 feet/

¹² S. Hersh, D. Donaldson, J. Kaufman, R. Hemingway, T. Becker, "Photographic Formulations for Machine Processing," ECOM Technical Report No. 3294, Photo Optics Tech Area, CS&TA Laboratory, ECOM, Fort Monmouth, NJ, February 1970.

¹³ "Processing Instructions for Use with Processing Machine, Photographic Film and Paper EH-29B," TB-11-6740-278-10/1, Dept of the Army, HQDA, Washington, D.C., August 1971.

minute 50 percent of the recoverable silver was carried into the two other processing tanks, approximately 30 percent of the undeveloped silver released from the film's emulsion was found in tank #3 and about 20 percent in tank #4. This information was quite disconcerting.

Apparently what is occurring at 7 feet/minute is a failure of the thiosulfate to remove the unexposed silver from the emulsion while the film is in the fixing tank. Thiosulfate evidently enters the softened emulsion, complexes with the unexposed silver forming $\text{Ag}(\text{S}_2\text{O}_3)^-$ but, because the residence time in the fixer tank is only about 30 seconds, the silver thiosulfate complex is not actually removed until the film passes into subsequent tanks. A quantity of rapid fix equivalent to 0.25 ounce per linear foot of film processed contains several times the quantity of thiosulfate required to carryout all of the silver that was found in the hypo clearing and wash water tanks (55 grams of silver found in tanks 3 and 4 after 200 feet of film processing). This substantiates to some extent the hypothesis for silver transfer stated above.

Extensive data on the quantity of silver which will be found in the hypo clearing tank and wash tank when processing at 1-1/2, 3 and 4-1/2 feet/minute is not yet available; however, the data that is available does indicate that even at slow processing speeds significant quantities of silver come into solution in the hypo clearing and wash water tanks. If the above hypothesis is correct, it is expected that as processing speed is decreased and, therefore, residence time in the rapid fix solution is increased, less silver will be found in the hypo clearing and wash water tanks.

In the tests run with photographic paper processed at 7 feet/minute, it was found that about 8 percent of the total silver which was fixed out of the paper was found in the hypo clearing tank and 1 percent in the wash water tank. It is concluded that fixing is much more effective when paper is processed at 7 feet/minute than when film is processed at that speed.

The possibility of using squeegees as a method for containing all of the silver in the fixing tank and for solving the carryout problem was considered. By placing squeegees between the tanks, the solutions would fall back into the "proper tanks." Such a modification results in a substantial redesign of the processing machine, because not only must the processing machine's "head" be modified to accommodate the squeegees, but the drive mechanism would have to be studied to see the effect of the increased friction on the take-up roller. The addition of squeegees also poses a number of other questions, such as: Will squeegees scratch the softened emulsion when it passes from developer to fix? Will squeegee action actually worsen fixing at high speeds by not allowing the continuation of fixing action in the hypo clearing tank, as appears to be occurring now? Will the squeegees need adjustment or replacement frequently? Based on the above and the significant costs required to accomplish the modification itself and the mechanical engineering study to see if such a modification were even feasible, it was determined that squeegees were not practical in the case of the EH-48B and should no longer be considered.

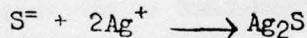
c. Sulfiding

Prior to modifying the processor, a total of 275 linear feet of 9-1/2 inch aerial film was processed. The processing machine was then converted to include an Argenta Model 30 electrolytic silver recovery unit in line with the EH-48B circulation system. This unit was connected in such a manner that a portion of the fixer would first be pumped through the silver recovery unit and then flow back into the tank. This arrangement permitted continuous desilvering of the fixing bath. Film was again processed at 7 feet/minute; a total of 375 feet was processed. Fixing became totally inadequate at approximately the 300 foot point. This apparently was not caused by excessive dilution of the fixer, but rather by sulfiding of the solution. Upon examining the fixing bath and the cathode surface, the presence of small black grains were detected; this was silver sulfide.

The formation of silver sulfide occurs when there are insufficient silver ions at the cathode. This happens when the silver ion concentration is too low for the current being applied between anode and cathode. The reaction is that of the decomposition of the thiosulfate ion,



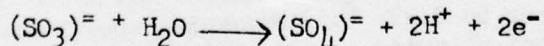
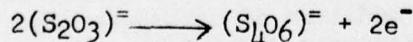
followed by the sulfide ion reacting with free silver ions in solution,



The potential for this reaction's occurrence is increased when the sulfite concentration is low; the low sulfite concentration drives the reaction to the right. The sulfite concentration needs to be maintained at about 10 grams/liter in order to get good silver plating.¹⁴

Sodium sulfite functions as a preservative in the fixing bath. Kodak has indicated that the normal concentration for this compound, when first produced by Kodak, is between 15 and 20 grams/liter. However, in functioning as a preservative, sulfite is oxidized to sulfate and, therefore, the actual concentration of sulfite, just prior to usage, is a function of time and storage conditions.

Additionally, sulfite is converted to sulfate at the anode during silver recovery. The two anode reactions are:



¹⁴ M. L. Schreiber, "Present Status of Silver Recovery in Motion Picture Laboratories - A Tutorial Paper," Journal Society of Motion Picture and Television Engineers, Vol. 74, p. 507, June 1965.

(It is noted that the thiosulfate ion concentration is also being reduced during the electrolytic silver recovery process.) During electrolysis 1.20 equivalents of sulfite ion and 1.21 equivalents of thiosulfate ion are lost per equivalent of silver recovered.¹⁵ Therefore, it would be necessary to add sodium sulfite to the ammonium thiosulfate fixer during hypo recirculation.

d. Recovery Capability

The "head" of the EH-48B processing machine has a plate on it which states that Plus-X Aerecon film should be processed at 7 feet/minute and Tri-X Aerecon film at 1-1/2 feet/minute.

Technical Bulletin 11-6740-278-10/1, although not recommending processing a 7 feet/minute, states that Plus-X Aerecon, as well as four other types of aerial film, can be processed at 5 feet/minute. Duplicating film and print paper are processed at 7 feet/minute, however, the silver content of these materials is significantly lower than aerial film and, therefore, they need not be considered in sizing a silver recovery unit.

Based on experiments run to date, it is estimated that 0.45 gram of silver will come into solution for every square foot of film processed. The Snook Corporation, manufacturer of ROTEX silver recovery units, uses a 0.5 gram/foot² factor in their design estimates. Kodak¹⁶ says to expect between 0.21 and 0.35 gram/foot² to be available for recovery. In specifying the capacity required the downtime should be considered; this is the time when a silver recovery unit might be running while no processing was occurring, thereby, letting the unit "catch up." The usual downtime occurs during machine threading and during chemical replenishments. Allowing for these downtimes, the capability of silver recovery units would have to be 3 troy ounces/hour recovery capability based on processing film at 5 feet/minute and 3-1/2 ounces/hour capacity at 7 feet/minute. (If recovery had to occur at the same rate as generation, it would be necessary to plate at the rate of 3-1/2 troy ounces/hour when processing at 5 feet/minute.)

Review of the commercial literature available from all electrolytic silver recovery unit manufacturers indicates that the 2 to 3 troy ounces/hour recovery capability unit is of moderate size (on the average 2 feet³ in overall volume), whereas once this recovery rate is exceeded, the next size unit up the manufacturer's product lines has a far greater capacity and a much larger size. It is noted that recovery capacities claimed by manufacturers represent the maximum capability of the unit. Maximum capacity is

¹⁵

A. A. Rasch & J. L. Crabtree, "Electrolytic Recovery of Silver from Fixing Baths at Low Current Density," Photographic Science & Technology, Vol. 2, pages 15-33, February 1955.

¹⁶

"Recovering Silver from Photographic Materials," Kodak Pamphlet No. J-10, Eastman-Kodak Co., Rochester, NY, page 8, 1969.

obtained at solution silver concentration of greater than 1 gram/liter and at a fixer pH of 4.5. The EH-29B would be operating at or near these conditions.

Fixer pH measurements are approximately 4.5. Ammonium thiosulfate solutions tolerate higher current and, therefore, silver can be plated more efficiently from them than from sodium thiosulfate fixers.¹⁷ A pH range of 4.0 to 6.5 is optimum for use of the metallic replacement cartridge; an acid solution is needed to etch the ferrous surface and, thereby provide new surface area for the continuance of the chemical reaction.¹⁸

4. ANALYSIS OF RESULTS

a. Alternatives

There are two methods of fixer silver recovery available for use in the ES-38B metallic replacement and electrolysis. The electrolytic recovery approach can be sub-divided into three alternatives: (a) a continuously recirculating system which would keep the silver concentration in the fixer tank at a constant level, (b) a tailing system which would remove silver from exhausted hypo just prior to final disposal, and (c) a continuously recirculating and tailing combination system. Because of the carryout condition discussed above, the possibility of treating the fixer, hypo clearing bath and wash water by either the metallic replacement or electrolytic methods in order to recover any silver carried out of the fixing bath, is also to be considered and is discussed below.

b. Recovery from Combined Solutions

Recovery of silver from any solutions other than the rapid fix would require a large volume of liquid to be treated in a relatively short time. The fix and hypo clearing tanks each hold 5 gallons of liquid and the wash water tank holds 8 gallons. This means that when the processor is to be totally drained and then refilled for additional processing, 18 gallons of liquid would have to be pumped to a holding tank for treatment if the three tanks were to be desilvered and 10 gallons if just the rapid fix and hypo clearing tanks were to be desilvered. A storage capacity to handle these volumes would be required for both EH-29B processors; the space required for such an operation is not available within the confines of the ES-38B.

A dump of the rapid fix, hypo clearing, and wash water tanks could contain up to 8 troy ounces of silver which would have to be recovered in less than 2 hours; this represents an extremely high recovery rate. Achievement of this recovery rate is made more difficult by the fact that metallic

¹⁷ M.L. Schreiber, "Present Status of Silver Recovery in Motion-Picture Laboratories - A Tutorial Paper," Journal Society of Motion-Picture and Television Engineers, Vol. 74, p. 507, Jun 1965.

¹⁸ "Recovering Silver from Photographic Materials," Kodak Pamphlet No. J-10, Eastman-Kodak Co., Rochester, NY, p. 10, 1972.

replacement and electrolytic methods are far less efficient in desilvering solutions of a higher pH than experienced in normal fixing baths. This would be the case in treating the hypo clearing bath (pH approximately 8), the wash water (pH approximately 7), or a combined effluent of rapid fix, hypo clearing bath and wash water (pH approximately 6.5). Higher pH's will require longer residence times in the unit in order to get adequate silver recovery. ES-38B mission requirements constrain the amount of time available for the desilvering process to occur and the attention the operator can give to the process.

Based on the above, it has been concluded that recovery of silver from solutions other than the rapid fix is not possible within the ES-38B due to space and mission requirements. If removal of silver not present in the rapid fix tank is required prior to final discharge in order to meet environmental regulations, it will have to be accomplished in a system placed external to the shelter. It is unlikely that recovery of the silver carried out of the rapid fix tank could be accomplished profitably. Additional data on (a) a silver carryout at film processing speeds other than 7 feet/minute and (b) silver recovery unit efficiency is needed to determine the amount of silver which will not be recovered. Because significant quantities of unrecovered silver dumped from the ES-38B are ecologically damaging, this situation needs to be addressed in overall pollution abatement with another product improvement effort.

c. Hypo Saving

Data obtained indicates that fixer life extension during film processing is not feasible. At 7 feet/minute the concentration of silver in the rapid fix tank is not the limiting parameter in clearing capability--dilution caused by developer carry-in is.

At lower speeds the film has more residence time in the fix tanks and, therefore, is more tolerable to build-ups of contaminants. It is possible, therefore, that some life extension when processing at 1-1/2 to 5 feet/minute may be obtained; however, because of the magnitude of the developer carried-in, it is not expected that much of an extension of hypo life is possible.

Even though hypo savings may be obtained in some film processing, the amount of information which the operator will need to keep in mind is likely to be confusing. The replenishment guidance provided would have to be in the form of a processing speed versus replenishment; the operator will still be required to follow the presently prescribed schedule for developer, hypo clearing bath, and wash water replenishment. Changes to the present system of replenishment do not appear to be practical.

As discussed above, when silver is plated from a thiosulfate bath, it is necessary to ensure a sulfite concentration of at least 10 grams/liter. The cost of sulfite will partially offset any cost saving obtained from increasing hypo life. Electrolytic silver recovery may actually result in a cost increase when hypo life is not increased but sulfite costs are incurred.

A recirculating silver recovery system will require the initial volume of rapid fix introduced into the processor to be increased in order to keep both the processor and the silver recovery unit at the prescribed level. If the silver recovery unit has a 5 gallon capacity, in order to break even with the present system in terms of the quantity of rapid fix used, no replenishment can be made for 1200 linear feet (948 square feet). The 1200 foot point calls for a complete refill of all tanks; it is reasonable to assume that dilution, dirt buildup, and contaminant buildup in the fixer would be significant enough at this point to warrant hypo drain out and refill.

In view of these facts, it is concluded that in the case of the ES-38 hypo life extension and, therefore, hypo cost saving cannot be achieved by utilizing an electrolytic silver recovery system. Further, a major disadvantage of the continuously recirculating electrolytic system is its potential for catastrophic failure. This would occur if the unit sulfided during processing; and the result would be a poisoned fixing bath and a ruined roll of film. Electrolytically recovering silver from hypo solutions during processing, therefore offers no benefit in the case of the ES-38B. The analysis that follows will be a comparison of the metallic replacement cartridge versus an electrolytic unit used as a tailing system.

d. Cost Analysis

For the purposes of analysis, the electrolytic system chosen for comparison with the metallic replacement cartridge will be a unit capable of recovering 3 troy ounces of silver/hour. The unit will be equipped with an automatic silver concentration sensor and corresponding current regulation device. The automatic current regulator will alleviate the operator of the job of current adjustment; if the sensing device were not available, the operator would have to set the current as a function of the number of square feet of material processed and as a function of the type of material being processed, i.e., aerial film, duplicating film, or paper. Based on the commercial data available and discussions with silver recovery equipment manufacturers, it is estimated that such a unit would cost \$1200. To this figure an additional \$200 for a processor interface should be added, totaling \$1400.

The metallic replacement cartridge with plastic holding tank, tubing and orifice will cost \$60. It is estimated that the modification package for this system would be similar to that for the electrolytic system, bringing the total cost to \$260. In the case of the cartridge, frequent replacement is necessary due to the exhaustion of the ferrous filler.

Kodak estimates the volume of solution that is needed to exhaust a cartridge is 220 gallons.¹⁹ Based on the utilization data provided by ECOM

¹⁹ "Silver Recovery with the Kodak Chemical Recovery Cartridge Type P and Type 3," Kodak Pamphlet No. J-9, Eastman Kodak Company, Rochester, NY, p. 11, March 1972.

Maintenance Engineering, a cartridge is expected to last 4 months before its exhaustion point is reached. The replacement cost of a cartridge is \$15.00 (based on the Kodak June 75 GSA Schedule), making the yearly replacement cost \$45.00.

The other major cost to consider is that of shipping. A filled cartridge weighs 60 lbs. Based on data provided by Earle Naval Depot,²⁰ the average shipping cost of a cartridge from any region in the United States to Earle Depot in New Jersey is \$10. Several ES-38's are located overseas and, therefore, in some instances, cartridges will first have to be transported back to the US and then forwarded to Earle. Mr. Sakowski, the Supply Management Officer at Earle, responsible for the silver reclamation program, has indicated that there are no shipping charges attached to cartridges coming in from overseas. The reason being that planes go over loaded with hardware and then have to fly back empty, and so arrangements are easily made to get cartridges back to the States. The shipping costs per cartridge on a yearly basis are, therefore, expected to be \$30.00.

Based on (a) field data which estimates yearly fixer usage to be 600 gallons per year per ES-38, (b) the assumption that the footage of film processed yearly is equivalent to the footage of paper processed yearly, and (c) an 80 percent overall system recovery efficiency, 25 lbs of silver would be recovered from the electrolytic process every year. This represents a mailing cost, including the insuring of the contents for their full value, of \$10.00 yearly. It is assumed that shipping from overseas of pure silver recovered electrolytically is also accomplished at no cost.

Estimates of the costs involved in maintaining an electrolytic system, in providing spare parts, and in establishing a maintenance float of several units have not been made and are, therefore, not included. Periodic maintenance, as well as calibration of the electronic sensor, will be required for the electrolytic system. In the case of the metallic replacement cartridge, this item is in the supply system and would be ordered as an expendable item by the field unit. The labor cost at depot for retrofitting ES-38's with silver recovery units is judged to be the same regardless of the type of recovery system employed and, therefore, this cost is not included in the analysis.

The comparison of costs over a 5 year life is shown in Table I. A 5 year life has been selected because it is expected that silver recovery system mod package can be fielded by FY-77, and by FY-82 the existing mobile photographic processing shelters will be replaced by the TIPL (Tactical Imagery Processing Laboratory). In order to bring future cost to present value, a 6 percent time-value of money factor has been employed. Utilizing the data in Table I (including the 6 percent time-value of money factor) the total expected cost over the 5 year period of an electrolytic system is \$1142 and the total expected cost of a metallic replacement system is \$576.

²⁰ W. Sakowski, "Reclamation of Silver from Scrap Material," Naval Ammunition Depot, Earle, Colts Neck, NJ, Sep 1970.

TABLE I
RECOVERY METHODS COST COMPARISON

	<u>ELECTROLYTIC</u>	<u>METALLIC REPLACEMENT</u>
Initial Cost	\$1400	\$260
Replacement Cost (yearly)	---	45
Shipping Cost (yearly)	<u>10</u>	<u>30</u>
Total Cost over a 5 year life (including 6% time-value of money factor)	\$1442	\$576

e. Recovery Method Comparison

There is no significant weight, size, or operator handling advantage for either system type. The space required for either a metallic replacement cartridge or for an electrolytic silver recovery system is about the same. An electrolytic unit and a 5 gallon cartridge are approximately the same size; the holding tank required for the cartridge system or the power unit and sensor of an electrolytic unit would have to be mounted in the same space on the shelf above the EH-29 processors.

Replacement of a cartridge would mean disconnecting two hose connections and then refitting the hoses on the new cartridge. Replacement of a cathode requires removing the fasteners from the cathode and then pulling the cathode out of the tank; this would be followed by drying, desilvering, and then cleaning with acetone. A filled cartridge weighs about 60 lbs, whereas a cathode with a month's load of silver weighs about 20 lbs. The entire electrolytic unit will most likely weigh more than a filled cartridge.

Although the fact that an electrolytic system produces silver in a high purity state is usually looked upon as an advantage to this system type, this is not the case in field operations. Use of an electrolytic unit may create a security problem. Because high purity silver is going to be handled prior to mailing to Earle Depot, the possibility of theft arises. A fully plated cathode would hold several hundred dollars worth of high purity silver. The cartridge, on the other hand, would present a far more difficult disposal problem for a would-be thief.

Another disadvantage of the electrolytic system is that it is far more complicated than the cartridge system. It is an electrical/mechanical system and as such can be expected to need preventive maintenance as well as occasional repair. The sensing device will need regular adjustment. The cartridge on the other hand, is a simple non-electrical, non-mechanical device which, when exhausted, is replaced with a new unit. The only attention it may require is an occasional cleaning of the cartridge discharge line with a bottle brush to ensure dried sludge is not blocking passage and forcing non-desilvered solution out through the by-pass.

The cartridge is not trouble free, however; one of the major problems associated with it is the reduced capacity associated with the intermittent usage. Kodak says: "Intermittent flow, such as dumping a tray or a 5 gallon container of chemical once a week, will produce a low total yield per cartridge because part of the steel wool is not available for the recovery function since some has oxidized. The normal life of a Kodak Chemical Recovery Cartridge under low volume, low use applications is approximately 6 months."²¹ This situation may result in some units getting less than a 220 gallon life out of the cartridge.

Associated with this problem of uncertain life is the need for the operator to frequently test the cartridge discharge to see whether silver is still being efficiently removed. Although this is easily done by using a silver estimating paper, it is another task which the operator must perform.

The metallic replacement cartridge releases iron into the discharge stream. Iron imparts a color and an odor to the waste stream if present in sufficient quantity. In the concentrations and quantities expected, this should have no environmental effect on a receiving stream. The cartridge functions by substituting an iron ion for two silver ions; the effluent will contain an iron concentration equivalent to 27 percent of what the silver concentration would be. For example, if the silver concentration were 1 gram/liter before installation of the cartridge and if all the silver were removed in the cartridge, the effluent would contain 0.27 gram/liter iron. It is estimated that the present effluent silver concentration is 2 grams/liter when film is being processed; assuming that at low processing speeds there is only a 5 percent carryout of silver from the fix tank and that the cartridge is on the average 90 percent efficient in recovering silver from the exhausted fix, this would mean the effluent would have a silver concentration of 0.30 gram/liter and an iron concentration of 0.46 gram/liter.

An important point, for which there presently is not enough data available to do a complete comparison, is the recovery efficiency at which the systems will operate. In the case of an electrolytic unit when used in the tailing mode, it is expected that the concentration at the unit overflow would be about 0.5 gram/liter. This means that 19 grams of silver plus whatever carryout occurs would be lost for every 1200 feet of film processed. The efficiency of the metallic replacement cartridge is not known. It is expected that initially the removal of silver will be extremely efficient, but as the volume of ferrous material within the cartridge decreases, the silver concentration exiting the cartridge will rise. The presence of silver at a concentration of 0.5 gram/liter is detectable by the use of silver estimating paper; at such a time the exhausted cartridge would be

²¹ "The Kodak Chemical Recovery Cartridge and Related Administrative Procedures," Kodak Supplement to Pamphlet J-9, Eastman-Kodak Co., Rochester, NY, p. 6, 1974.

replaced with a new one. The attention which the operator pays to the cartridge once approximately 200 gallons of fixer have been drained through it will affect the efficiency of removal actually achieved.

f. Economics of Silver Recovery

The total R&D, design, and modification cost for the ES-38 silver recovery effort on a per lab basis is approximately \$3000. Therefore, the investment by the Army for a metallic replacement system is \$3,260. The yearly cost associated with silver recovery utilizing this system is \$75 (this does not include the refining and handling costs incurred by Earle Depot). This expense is offset by the value of the silver recovered during the course of the year.

On the average 25 lbs. of silver will be recovered yearly. Assuming a market value of \$4.00 per troy ounce, this silver is worth \$1458. The revenues and expenses associated with this effort are summarized in Table II. Bringing the FY-78 through FY-82 expenses and revenues to their present value (again using a 6 percent factor) results in an expected net profit of \$2565. per ES-38 (\$6141. - \$3576.).

TABLE II
ES-38 SILVER RECOVERY CASH FLOW

	<u>INITIAL</u>	<u>78</u>	<u>78</u>	<u>80</u>	<u>81</u>	<u>82</u>	<u>TOTAL</u>
Expense (\$)	3260	75	75	75	75	75	3576
Revenue (\$)		1458	1458	1458	1458	1458	6141

5. CONCLUSIONS

The metallic replacement cartridge is the less expensive alternative with its expected life cycle cost being \$576 versus \$1442 for a typical electrolytic system. It offers a lower probability of field difficulties because it will be less of a security and maintenance problem. The metallic replacement cartridge does not present a greater size, weight, or operator attention problem than does an electrolytic system. In regard to efficiency, it is not expected that there will be a significant difference between system types. The possibility of reduced cartridge life due to intermittent usage of the shelter does exist; however, cartridge life would have to be reduced from 220 gallons, as is estimated by Kodak,²² to approximately 75 gallons in

²² "Silver Recovery with the Kodak Chemical Recovery Cartridge Type P and Type 3," Kodak Pamphlet No. J-9, Eastman-Kodak Co., Rochester, NY, p. 11, March 1972.

order to make the cartridge less cost effective than the electrolytic system. No adverse environmental effect is expected from the iron placed in solution by the metallic replacement cartridge. The quantity of silver that will be lost because of solution carryout will have a greater environmental impact than will the iron.²³ Should quantities of residual silver or silver and iron be considered too high, then pretreatment will be necessary by hardware located external to the mobile laboratory.

The major conclusions for application of silver recovery to the ES-38 are:

- a. Reductions in hypo consumption cannot be obtained by removing silver from fixer during processing.
- b. In-process silver recovery by a continuous recirculation mode of operation is impractical. Silver must be recovered in a tailing operation.
- c. The metallic replacement cartridge is the more cost effective alternative for a tailing system.
- d. Significant quantities of silver are carried into the hypo clearing and wash water tanks during processing. Recovery of this silver is not possible by hardware located within the confines of the shelter. The profitability of silver recovered from exhausted hypo clearing bath and from wash waters is doubtful.
- e. The revenues derived from silver recovery from exhausted rapid fix solutions will exceed all the costs incurred for that recovery; therefore, silver recovery will be profitable.

6. ACKNOWLEDGMENT

The assistance of Mr. Irving Bauman, Leader, Photographic Equipment Development Team, is gratefully acknowledged. His technical expertise and managerial guidance were a vital part of this product.

²³ "Proposed Criteria for Water Quality," US Environmental Protection Agency, Washington, D. C., Oct 1973.

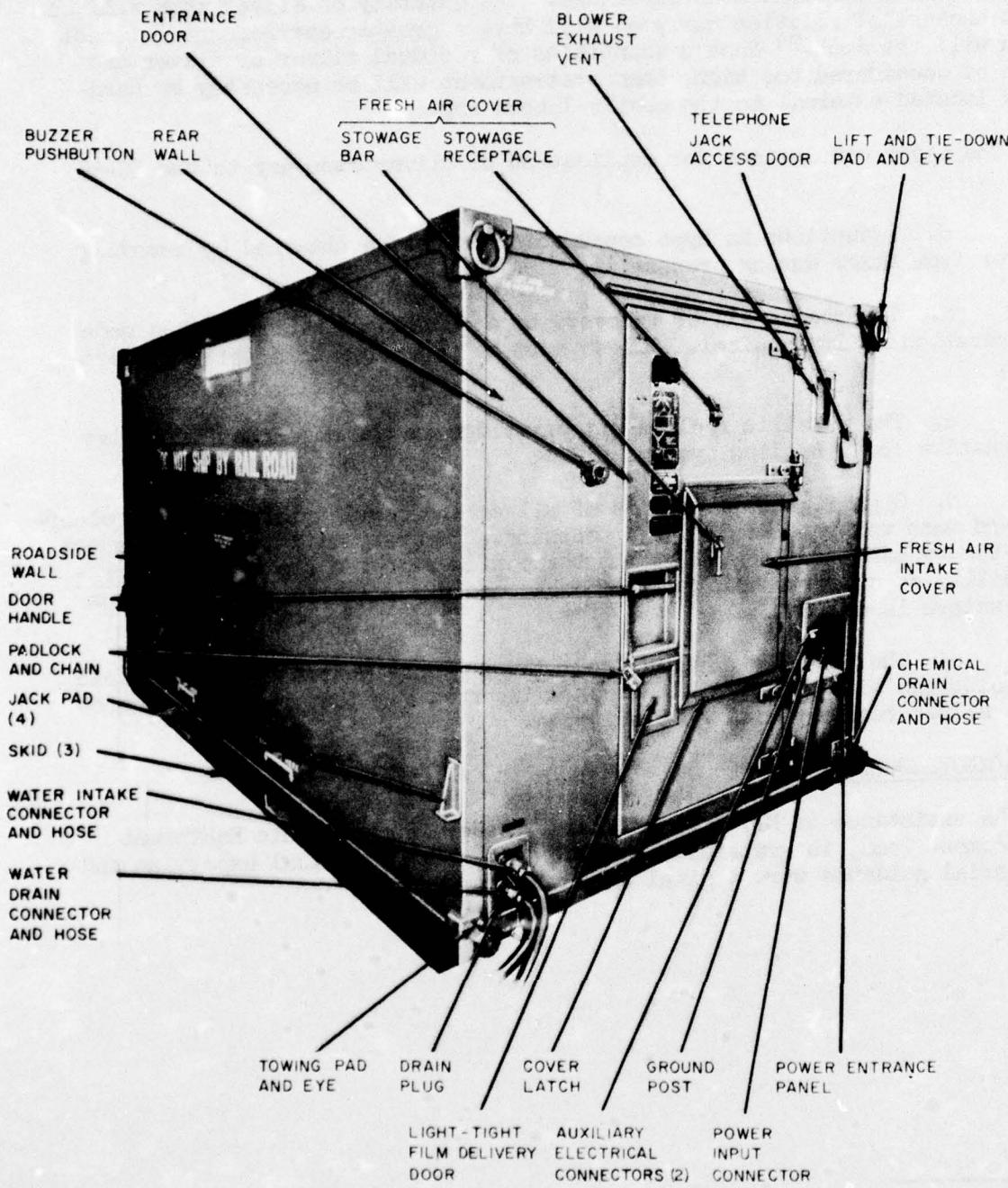


Figure 1. Outside View of the ES-38B Mobile Processing Laboratory

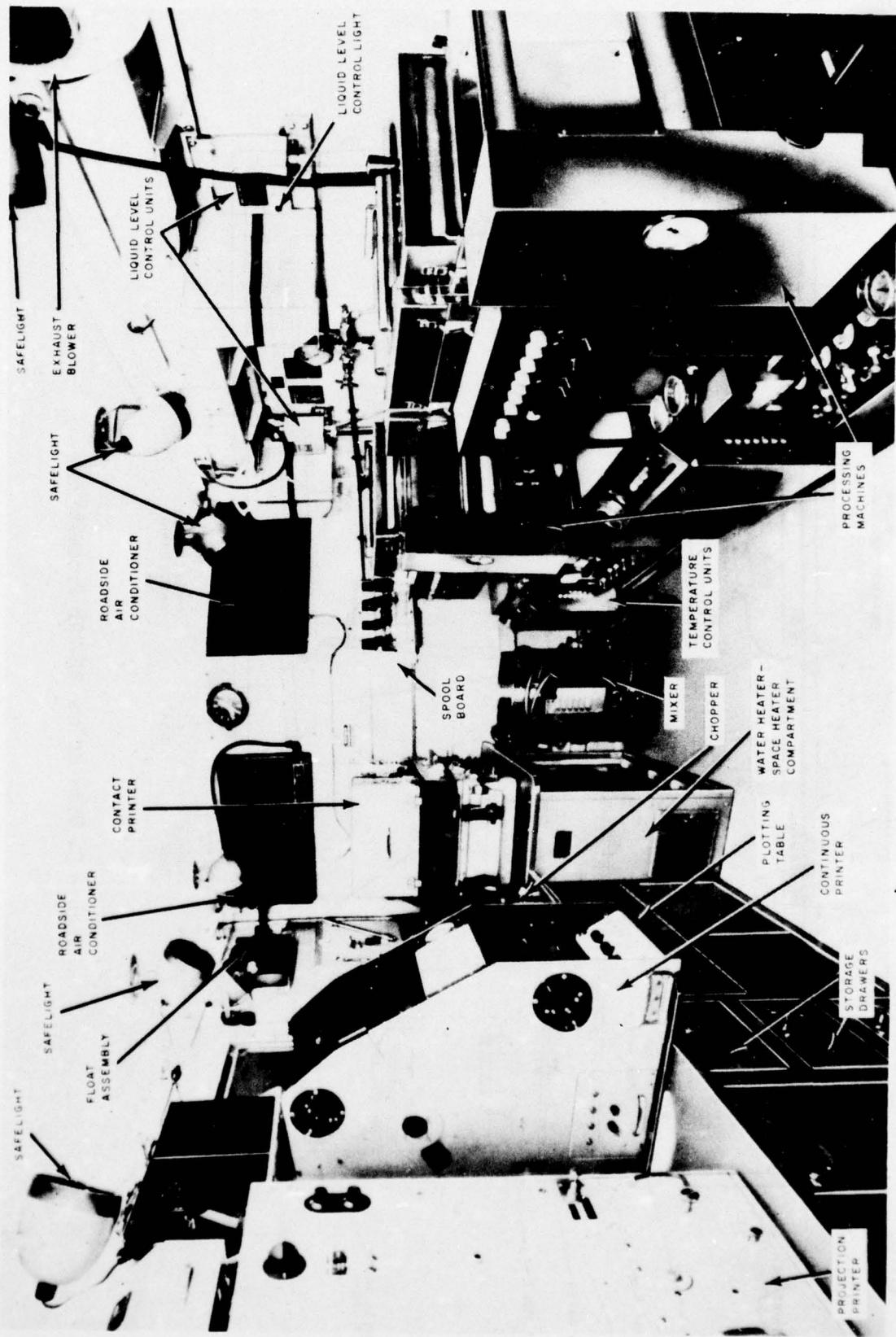


Figure 2. Inside View of the ES-38B Mobile Processing Laboratory

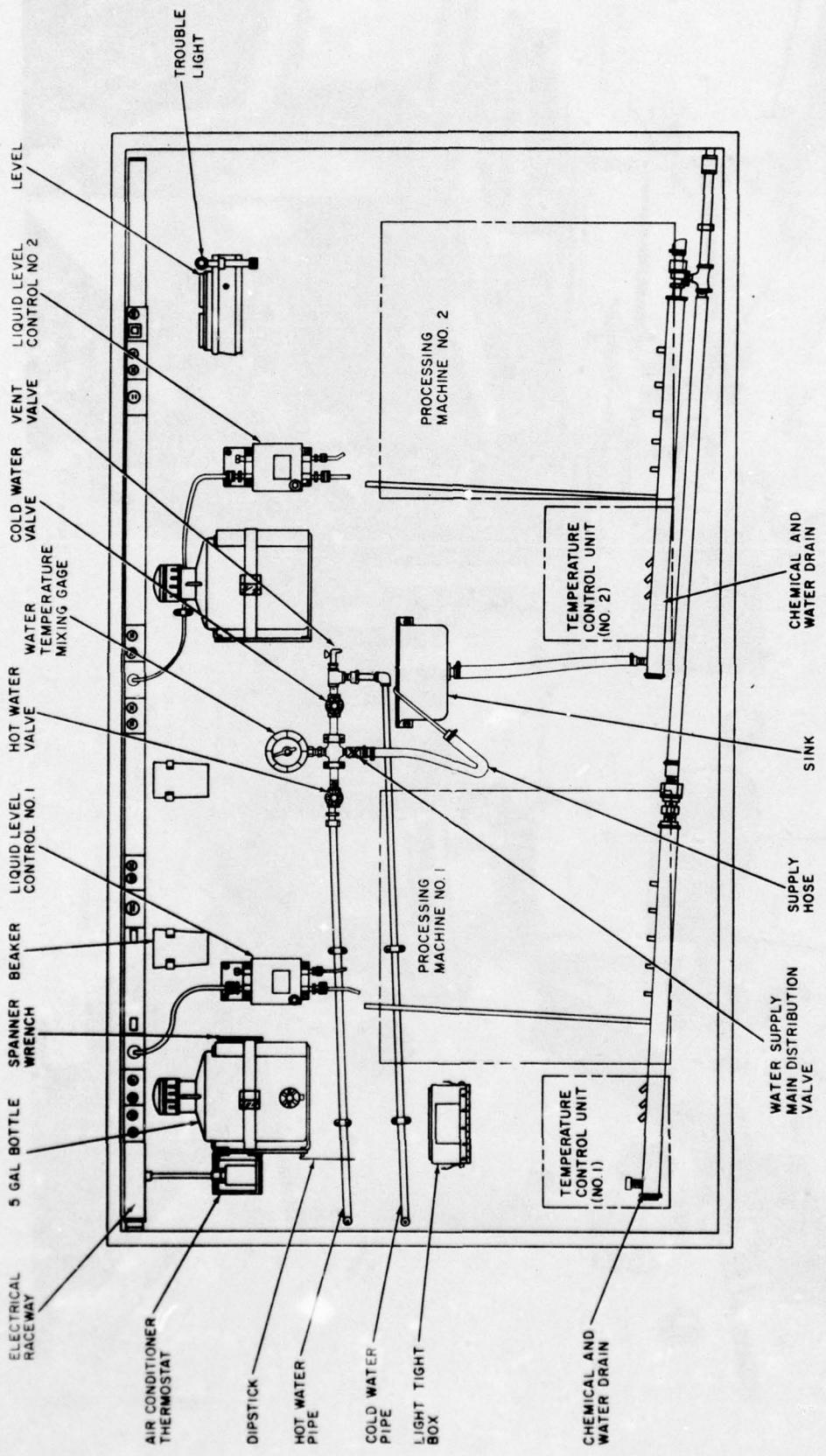


Figure 3. View of the EH-29B Processor